

## Arsenic species in groundwater in paddy fields with high soil arsenic content

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### Abstract

In total, 121 groundwater samples were collected from paddy fields in Chungwa, Yunlin, Chiayi, Tainan, Pingtung and Ilan counties in Taiwan. The concentrations of total arsenic, As(III), As(V), MMAA and DMAA in water samples were determined. Analytical results demonstrate that average total As content in groundwater samples from highest to lowest were as follows: Ilan (130 µg/L) > Chiayi (69.5 µg/L) > Tainan (30.8 µg/L) > Changhwa (10.8 µg/L) > Pingtung (0.44 µg/L). The percentages of samples with As content over the irrigation water arsenic standard of 50 µg/L were 48%, 8%, 50% and 29%, for Ilan, Changhwa, Chiayi and Tainan, respectively. The predominant As species in groundwater was arsenite (As(III)). The ratio of arsenite to total arsenic was 43.4–95.3%. However, both DMAA and the MMAA did not exist in all samples. Evaluation results reveal that the toxicity of As to rice is high; therefore, rice cannot be produced as As content exceeds maximum permissible limits in rice paddies.

**Key words:** arsenic speciation, arsenite (As(III)), arsenate (As(V)), dimethylarsinic acid (DMAA), monomethylarsonic acid (MMAA), groundwater

### Introduction

Arsenic and other metals, such as Be, Sb, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl, and Zn, are listed as “priority metals” in soils as they are potentially hazardous to human health (McBride, 1994). Black-foot disease endemic in south-west Taiwan results from long-term intake of groundwater contaminated with As (Tseng, 1977; Engel et al., 1994). Arsenic toxicity depends on the As forms present. The toxicities of arsenics from highest to lowest are as follows: arsenite (As(III)) > arsenate (As(V)) > organic arsenic (Farmer et al., 1989; Korte and Fernando, 1991). Abedin and Meharg (2002) reported that As(III) was more toxic than As(V) in terms of rice germination and shoot growth; however, As(V) was more toxic than As(III) to root growth. Based on data from the Environmental Protection Administration (Taiwan) (1991), high As content (> 15 mg/kg) was found in soil samples for Ilan, Changhwa, Yunlin, Chiayi, Tainan and Pingtung counties in Taiwan. This study investigates arsenic concentrations and species in groundwater in agricultural areas where soils have high arsenic content. The ratios of As(III) to total As were determined. Additionally, the safety of using groundwater as irrigation water was assessed.

### Materials and Methods

In total, 121 groundwater samples were collected from paddy fields in Ilan, Chungwa, Yunlin, Chiayi, Tainan and Pingtung counties (Fig. 1). The soils for Yunlin, Changhwa, Pingtung and Ilan counties were come from slate alluvial deposits, and the other soils were come from mixed sandstone and shale alluvial deposits. Groundwater was filtered through a 0.22-µm membrane (MILLEX<sup>®</sup>GS). Filtrates were then analyzed for arsenic species using high-performance liquid chromatography combined with inductively coupled plasma mass spectrometry (HPLC-ICPMS). An Agilent anion exchange resin (Hydrophilic polymethacrylate as the basic resin) was used to separate arsenic species. Tables 1 and 2 present the conditions for HPLC and ICPMS, respectively. A 15-mL sample of groundwater filtered through the 0.22-µm membrane (MILLEX<sup>®</sup>GS) and 15-mL of HCl were put into a reaction tube, and then reacted with an aqueous solution of 1% NaBH<sub>4</sub> and 1% NaOH. The amount of As was determined by a JOBIN-YVON JY-138 ULTRACE ICP-AES equipped with a hydride generator.

### Results and Discussion

Figure 2 presents chromatograms for As(III), DMAA, MMAA, and As(V). These chromatograms reveal that arsenic species were separated by gradient

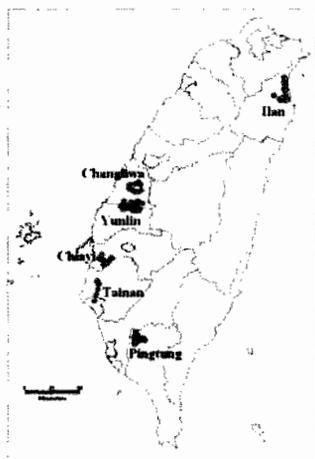


Fig. 1. Map showing location and sampling sites of groundwater samples

Table 1. Chromatographic conditions used for arsenic speciation analysis

HPLC	Agilent 1100
Column	Agilent anion exchange resin (Hydrophilic polymethacrylate as basic resin) Column material: PEEK1 Column size : G3154-65001: 4.6 mm x 150 mm i.d. G3154-65002: 4.6 mm x 10 mm i.d.
Mobile phase	2.0mM PBS / 0.2mM EDTA (pH6.0)
Column parameters	Injection volume: 100 uL Column pressure: 65-70 bar Column flow rate: 1.0mL/min Stop time: 10 min Post time: 5 min

Table 2. Instrumental conditions of the ICPMS

Parameter	Setting/Type
ICP-MS	Agilent 7500 ce
RF power	1500 W
Carrier gas	1 L/min
Makeup gas	0.2 L/min
Reaction gas	He at 3L/min
Nebulizer pump	0.2 rps
S/C temp.	2 °C
Monitored ion m/z	75( <sup>75</sup> As), 35 ( <sup>35</sup> Cl)
Dwell time	410 ms/mass
Total acquisition time	660 sec

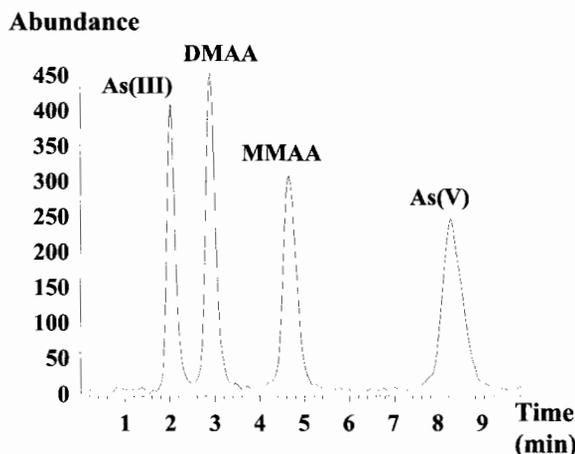


Fig. 2. Chromatogram of five different arsenic standards: As(III), DMAA, MMAA, and As(V), the concentration is 10 µg/L as As

anion exchange HPLC using the mobile phase of  $\text{NH}_4\text{H}_2\text{PO}_4$  and an EDTA mixed solution. Separation was completed in <10 min. High concentrations of naturally occurring As have been found in groundwater in Bangladesh, India, Taiwan, Chile, Mexico, Hungary, the USA, Argentina, and China (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002; Nordstrom, 2002; Kouras et al., 2007). The As concentrations in groundwater samples collected from areas with high soil As content worldwide are 0.001–48,000 µg/L (Mandal and Suzuki, 2002). Table 3 lists the total As content in groundwater samples. The average As content in groundwater samples from Ilan, Chiayi, Tainan, Changhua, Yunlin and Pingtung are 130, 69.5, 30.8, 10.8, 3.05 and 0.44 µg/L, respectively. The samples with high As concentrations (> 300µg/L) are all from Ilan county. Groundwater samples from Pingtung county has low As concentrations; only 7% of samples contained >2 µg/L As, and the remaining samples had As concentrations <0.5 µg/L. The drinking water standard for As to protect human health in some countries is 10 µg/L (WHO, 2001; Smith et al., 2002; Environmental Protection Administration (Taiwan), 2005). Irrigation water, not drinking water, was sampled in this study. The irrigation water standard for As established by the Council of Agriculture, Taiwan, is 50 µg/L (Council of Agriculture, 2003). No samples from Pingtung and Yunlin counties had As concentrations that exceeded the irrigation water standard of 50 µg/L. However, the ratio of samples with As concentrations exceeding 50 µg/L collected in Chiayi, Tainan, and Changhua counties are 50%, 29% and 8%, respectively. The high concentration of As in irrigation water may pose risk to irrigated crops.

The As(III) content in samples from Pingtung County were undetectable. The average As(III) concentrations in samples from Ilan, Chiayi, Tainan,

Changhwa and Yunlin counties were 66.2 µg/L, 58.0 µg/L, 28.1 µg/L, 9.54 µg/L and 2.87 µg/L, respectively (Table 3). The percentage of As(III) to total As in all samples (except samples collected from Pingtung County) was 43.4–95.3% (Table 3). Furthermore, monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) in all samples were undetectable. The experimental results demonstrate that the major arsenic species in groundwater is inorganic As(III). Groundwater samples taken from 73 wells in 10 counties in southern Michigan in 1997 had arsenic concentrations of 0.5–278 µg/L (average, 29 µg/L). Most (53–98%) of arsenic detected was arsenite (As(III)) (Kim et al., 2002). The As(III) in groundwater accounted for about 50% of total As in arsenic-affected areas in West Bengal, India (Chatterjee, 1995). Moreover, As(III) accounted for 50–60% of total As in arsenic-affected areas in Bangladesh (Mandal and Suzuki, 2002). The As(V) in samples collected at Yunlin County was undetectable. Comparing the average ratio of As(V) to total As in different samples demonstrates that samples collected from Pingtung County have higher ratios of As(V) to total As than samples from other areas. This area has

a shallow groundwater level that keeps water in an aerobic condition; thus, the predominant As species was As(V).

Abedin et al., (2002a; b) reported that using irrigation water with a high As content (8 mg/L) reduced plant height, rice yield and root growth. However, the As concentration in rice did not exceed the maximum permissible limit of 1.0 mg/kg. Moreover, for areas in Bangladesh, As concentrations in groundwater was 2 mg/L and 83 mg/kg in soil. However, the As content in rice grains did not exceed 1.0 mg/kg (Hossain, 2006). In the study by Li and Fei (1980), the As concentration in unpolished rice was proportionally increased as As levels in soil increased. But, 100% empty rice grains were caused when As concentration was sufficiently high to produced rice grains with high As content. Therefore, the As concentration in their study did not exceed 2 mg/kg. Based on above results, that the toxicity of As to rice is high; therefore, rice cannot be produced as As content exceeds maximum permissible limits in rice paddies.

Table 3. Content of total As and arsenic species in groundwater samples (µg/L)<sup>a</sup>

Areas	Total As	As(III)	As(V)	As(III)/Total As (%)
Ilan (27)	130±50 <sup>b</sup> (0.17-430) <sup>c</sup>	66.2±107 (<0.5-347)	65.3±104 (<1-364)	43.4 (0-80.2)
Changhwa (24)	10.8±19.5 (<0.5-75.2)	9.54±16.7 (<0.5-67.2)	0.71±1.83 (<1-8.00)	95.3 (84.5-100)
Yunlin (17)	3.05±2.27 (<0.5-6.76)	2.87±2.24 (<0.5-6.76)	<1	94.7 (85.0-100)
Chiayi (16)	69.5±48.8 (9.90-213)	58.0±41.5 (7.90-180)	5.90±7.31 (<1-23.3)	86.3 (71.0-97.1)
Tainan (7)	30.8±23.0 (<0.5-53.1)	28.1±21.9 (<0.5-50.6)	2.97±5.21 (<1-12.4)	90.8 (71.1-100)
Pingtung (27)	0.44±0.47 (<0.5-2.44)	<0.5	0.36±0.40 (<1-2.12)	--

<sup>a</sup>DMAA, MMAA were undetectable.

<sup>b</sup>Data are mean±standard deviations

<sup>c</sup> Range.

### Conclusions

The average As content in groundwater samples collected from paddy fields with soil arsenic content from highest to lowest were: Ilan (130 µg/L) > Chiayi (69.5 µg/L) > Tainan (30.8 µg/L) > Changhwa (10.8 µg/L) > Pingtung (0.44 µg/L). The samples with high As concentrations (> 300 µg/L) are all from Ilan County. No samples from Pingtung and Yunlin counties had As concentrations that exceeded the irrigation water standard of 50 µg/L. However, the ratios of samples with As concentrations exceeding 50 µg/L collected from Chiayi, Tainan, and Changhwa counties were 50%, 29% and 8%,

respectively. The predominant As compound in groundwater samples was As(III). Both MMAA and DMAA were undetectable in groundwater samples. Evaluation results reveal that the toxicity of As to rice is high; therefore, rice cannot be produced as As content exceeds maximum permissible limits. However, attention should be paid to the effects of irrigation water contaminated with As on rice production.

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